14 Chemical Kinetics

Visualizing Concepts

14.1  
(a) X is a product, because its concentration increases with time.

(b) The average rate of reaction between any two points on the graph is the slope of the line connecting the two points. The average rate is greater between points 1 and 2 than between points 2 and 3 because they are different stages in the overall process. Points 1 and 2 are earlier in the reaction when more reactants are available, so the rate of formation of products is greater. As reactants are used up, the rate of X production decreases, and the average rate between points 2 and 3 is smaller.

14.4 Analyze. Given three mixtures and the order of reaction in each reactant, determine which mixture will have the fastest initial rate.

Plan. Write the rate law. Count the number of reactant molecules in each container. The three containers have equal volumes and total numbers of molecules. Use the molecule count as a measure of concentration of NO and O$_2$. Calculate the initial rate for each container and compare.

Solve. Rate = k[NO]$^2$[O$_2$]; rate is proportional to [NO]$^2$[O$_2$]

<table>
<thead>
<tr>
<th>Container</th>
<th>[NO]</th>
<th>[O$_2$]</th>
<th>[NO]$^2$[O$_2$] ≈ rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>5</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>(2)</td>
<td>7</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>(3)</td>
<td>3</td>
<td>6</td>
<td>54</td>
</tr>
</tbody>
</table>

The relative rates in containers (1) and (2) are very similar, with (1) having the slightly faster initial rate.

14.6 Analyze. Given concentrations of reactants and products at two times, as represented in the diagram, find $t_{1/2}$ for this first-order reaction.

Plan. For a first order reaction, $t_{1/2} = 0.693/k$; $t_{1/2}$ depends only on $k$. Use Equation [14.12] to solve for $k$. Solve.

(a) Since reactants and products are in the same container, use number of particles as a measure of concentration. The red dots are reactant A, and the blue are product B. $[A]_0 = 8$, $[A]_{30} = 2$, $t = 30$ min.

\[
\ln \left( \frac{[A]_0}{[A]} \right) = -kt. \quad \ln(2/8) = -k(30 \text{ min}); \quad \frac{-1.386}{30\text{min}} = k;
\]
k = 0.046210 = 0.0462 min\(^{-1}\)

t\(_{1/2}\) = 0.693/k = 0.693/0.046210 = 15 min

By examination, \([A]_0 = 8, \ [A]_\infty = 2\). After 1 half-life, \([A] = 4\); after a second half-life, \([A] = 2\). Thirty minutes represents exactly 2 half-lives, so \(t_{1/2} = 15\) min. [This is more straightforward than the calculation, but a less general method.]

(b) After 4 half-lives, \([A] = [A]_0 \times 1/2 \times 1/2 \times 1/2 \times 1/2 = [A]_0/16\). In general, after \(n\) half-lives, \([A] = [A]_0/2^n\).

14.10 This is the profile of a two-step mechanism, \(A \rightarrow B\) and \(B \rightarrow C\). There is one intermediate, \(B\). Because there are two energy maxima, there are two transition states. The \(B \rightarrow C\) step is faster, because its activation energy is smaller. The reaction is exothermic because the energy of the products is lower than the energy of the reactants.

**Reaction Rates**

14.13 (a) *Reaction rate* is the change in the amount of products or reactants in a given amount of time; it is the speed of a chemical reaction.

(b) Rates depend on concentration of reactants, surface area of reactants, temperature and presence of catalyst.

(c) The stoichiometry of the reaction (mole ratios of reactants and products) must be known to relate rate of disappearance of reactants to rate of appearance of products.

14.15 *Analyze/Plan.* Given mol \(A\) at a series of times in minutes, calculate mol \(B\) produced, molarity of \(A\) at each time, change in \(M\) of \(A\) at each 10 min interval, and \(\Delta M\ A/s\). For this reaction, mol \(B\) produced equals mol \(A\) consumed. \(M\) of \(A\) or \([A]\) = mol \(A\)/0.100 L. The average rate of disappearance of \(A\) for each 10 minute interval is

\[
\frac{-\Delta[A]}{s} = -\frac{[A]_i - [A]_f}{10\text{min}} \times \frac{1\text{min}}{60\text{s}}
\]

*Solve.*

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mol A</th>
<th>(a) Mol B</th>
<th>[A]</th>
<th>(\Delta [A])</th>
<th>(b) Rate (-\Delta [A]/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.065</td>
<td>0.000</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.051</td>
<td>0.014</td>
<td>0.51</td>
<td>-0.14</td>
<td>(2.3 \times 10^{-4})</td>
</tr>
<tr>
<td>20</td>
<td>0.042</td>
<td>0.023</td>
<td>0.42</td>
<td>-0.09</td>
<td>(2 \times 10^{-4})</td>
</tr>
<tr>
<td>30</td>
<td>0.036</td>
<td>0.029</td>
<td>0.36</td>
<td>-0.06</td>
<td>(1 \times 10^{-4})</td>
</tr>
<tr>
<td>40</td>
<td>0.031</td>
<td>0.034</td>
<td>0.31</td>
<td>-0.05</td>
<td>(0.8 \times 10^{-4})</td>
</tr>
</tbody>
</table>

(c) \[
\frac{\Delta M_B}{\Delta t} = \frac{(0.02\cdot0.014)\text{mol}/0.10\text{L}}{(30-10)\text{min}} \times \frac{1\text{min}}{60\text{s}} = 1.25 \times 10^{-4} = 1.3 \times 10^{-4} \text{M/s}
\]
Chemical Kinetics

Solutions to Exercises

14.17 (a) *Analyze/Plan.* Follow the logic in Sample Exercises 14.1 and 14.2. *Solve.*

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Time Interval (sec)</th>
<th>Concentration (M)</th>
<th>ΔM</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2,000</td>
<td>0.0165</td>
<td>-0.0055</td>
<td>28 × 10⁻⁷</td>
</tr>
<tr>
<td>2,000</td>
<td>2,000</td>
<td>0.0110</td>
<td>-0.0051</td>
<td>17 × 10⁻⁷</td>
</tr>
<tr>
<td>5,000</td>
<td>3,000</td>
<td>0.00591</td>
<td>-0.00277</td>
<td>9.23 × 10⁻⁷</td>
</tr>
<tr>
<td>8,000</td>
<td>3,000</td>
<td>0.00314</td>
<td>-0.00177</td>
<td>4.43 × 10⁻⁷</td>
</tr>
<tr>
<td>12,000</td>
<td>4,000</td>
<td>0.00137</td>
<td>-0.00063</td>
<td>2.1 × 10⁻⁷</td>
</tr>
<tr>
<td>15,000</td>
<td>3,000</td>
<td>0.00074</td>
<td>-0.00063</td>
<td>2.1 × 10⁻⁷</td>
</tr>
</tbody>
</table>

(b) From the slopes of the lines in the figure at right, the rates are:
- at 5000 s, 12 × 10⁻⁷ M/s;
- at 8000 s, 5.8 × 10⁻⁷ M/s

14.19 *Analyze/Plan.* Follow the logic in Sample Exercise 14.3. *Solve.*

(a) \(-\Delta[H_2O]/\Delta t = \Delta[H_2]/\Delta t = \Delta[O_2]/\Delta t\)

(b) \(-\Delta[N_2O]/2\Delta t = \Delta[N_2]/2\Delta t = \Delta[O_2]/\Delta t\)

\(-\Delta[N_2O]/\Delta t = \Delta[N_2]/\Delta t = 2\Delta[O_2]/\Delta t\)

(c) \(-\Delta[N_2]/\Delta t = \Delta[NH_3]/2\Delta t; -\Delta[H_2]/3\Delta t = \Delta[NH_3]/2\Delta t\)

\(-2\Delta[N_2]/\Delta t = \Delta[NH_3]/\Delta t; -\Delta[H_2]/\Delta t = 3\Delta[NH_3]/2\Delta t\)

14.21 *Analyze/Plan.* Use Equation [14.4] to relate the rate of disappearance of reactants to the rate of appearance of products. Use this relationship to calculate desired quantities. *Solve.*

(a) \(\Delta[H_2O]/2\Delta t = -\Delta[H_2]/2\Delta t = -\Delta[O_2]/\Delta t\)

H₂ is burning, \(-\Delta[H_2]/\Delta t = 0.85 \text{ mol/s}\)

O₂ is consumed, \(-\Delta[O_2]/\Delta t = -\Delta[H_2]/2\Delta t = 0.85 \text{ mol/s}/2 = 0.43 \text{ mol/s}\)
H₂O is produced, \( +\Delta[H₂O]/\Delta t = -\Delta[H₂]/\Delta t = 0.85 \text{ mol/s} \)

(b) The change in total pressure is the sum of the changes of each partial pressure. NO and Cl₂ are disappearing and NOCl is appearing.

\[ -\Delta P_{\text{NO}}/\Delta t = 23 \text{ torr/min} \]
\[ -\Delta P_{\text{Cl₂}}/\Delta t = \Delta P_{\text{NO}}/2\Delta t = -12 \text{ torr/min} \]
\[ +\Delta P_{\text{NOCl}}/\Delta t = -\Delta P_{\text{NO}}/\Delta t = +23 \text{ torr/min} \]
\[ \Delta P_T/\Delta t = -23 \text{ torr/min} - 12 \text{ torr/min} + 23 \text{ torr/min} = -12 \text{ torr/min} \]

**Rate Laws**

14.23 *Analyze/Plan.* Follow the logic in Sample Exercises 14.4 and 14.5. *Solve.*

(a) If \([A]\) is doubled, there will be no change in the rate or the rate constant. The overall rate is unchanged because \([A]\) does not appear in the rate law; the rate constant changes only with a change in temperature.

(b) The reaction is zero order in \(A\), second order in \(B\) and second order overall.

(c) Units of \(k = \frac{M}{s} = M^{-1}s^{-1}\)

14.25 *Analyze/Plan.* Follow the logic in Sample Exercise 14.4. *Solve.*

(a) \(\text{rate} = k[N₂O₅] = 4.82 \times 10^{-3} \text{ s}^{-1} [N₂O₅] \)

(b) \(\text{rate} = 4.82 \times 10^{-3} \text{ s}^{-1} (0.0240 \text{ M}) = 1.16 \times 10^{-4} \text{ M/s} \)

(c) \(\text{rate} = 4.82 \times 10^{-3} \text{ s}^{-1} (0.0480 \text{ M}) = 2.31 \times 10^{-4} \text{ M/s} \)

When the concentration of \(N₂O₅\) doubles, the rate of the reaction doubles.

14.27 *Analyze/Plan.* Write the rate law and rearrange to solve for \(k\). Use the given data to calculate \(k\), including units. *Solve.*

(a, b) \(\text{rate} = k[\text{CH₃Br}][\text{OH}^-]\); \(k = \frac{\text{rate}}{[\text{CH₃Br}][\text{OH}^-]} \)

at 298K, \(k = \frac{0.043 M/s}{(5.0 \times 10^{-3} M)(0.05 M)} = 1.7 \times 10^2 M^{-1}s^{-1} \)

(c) Since the rate law is first order in \([\text{OH}^-]\), if \([\text{OH}^-]\) is tripled, the rate triples.

14.29 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6. *Solve.*

(a) From the data given, when \([\text{OCl}^-]\) doubles, rate doubles. When \([\text{I}^-]\) doubles, rate doubles. The reaction is first order in both \([\text{OCl}^-]\) and \([\text{I}^-]\). \(\text{rate} = [\text{OCl}^-][\text{I}^-] \)

(b) Using the first set of data:

\( k = \frac{\text{rate}}{[\text{OCl}^-][\text{I}^-]} = \frac{1.36 \times 10^4 M/s}{(1.5 \times 10^{-3} M)(1.5 \times 10^{-3} M)} = 60.444 = 60 M^{-1}s^{-1} \)
14.31 Analyze/Plan. Follow the logic in Sample Exercise 14.6 to deduce the rate law. Rearrange the rate law to solve for \( k \) and deduce units. Calculate a \( k \) value for each set of concentrations and then average the three values. Solve.

(a) Doubling \([\text{NH}_3]\) while holding \([\text{BF}_3]\) constant doubles the rate (experiments 1 and 2). Doubling \([\text{BF}_3]\) while holding \([\text{NH}_3]\) constant doubles the rate (experiments 4 and 5).

Thus, the reaction is first order in both \( \text{BF}_3 \) and \( \text{NH}_3 \); rate = \( k[\text{BF}_3][\text{NH}_3] \).

(b) The reaction is second order overall.

(c) From experiment 1: \( k = \frac{0.213 \text{ M/s}}{(0.25 \text{ M})(0.25 \text{ M})} = 3.41 \text{ M}^{-1} \text{ s}^{-1} \)

(Any of the five sets of initial concentrations and rates could be used to calculate the rate constant \( k \). The average of these 5 values is \( k_{\text{avg}} = 3.408 = 3.41 \text{ M}^{-1} \text{ s}^{-1} \))

(d) \( \text{rate} = 3.41 \text{ M}^{-1} \text{ s}^{-1}(0.100 \text{ M})(0.500 \text{ M}) = 0.1704 = 0.170 \text{ M/s} \)

14.33 Analyze/Plan. Follow the logic in Sample Exercise 4.6 to deduce the rate law. Rearrange the rate law to solve for \( k \) and deduce units. Calculate a \( k \) value for each set of concentrations and then average the three values. Solve.

(a) Increasing \([\text{NO}]\) by a factor of 2.5 while holding \([\text{Br}_2]\) constant (experiments 1 and 2) increases the rate by a factor 6.25 or \((2.5)^2\). Increasing \([\text{Br}_2]\) by a factor of 2.5 while holding \([\text{NO}]\) constant increases the rate by a factor of 2.5. The rate law for the appearance of \( \text{NOBr} \) is: rate = \( \frac{\Delta[\text{NOBr}]}{\Delta t} = k[\text{NO}]^2[\text{Br}_2] \).

(b) From experiment 1: \( k_1 = \frac{24 \text{ M/s}}{(0.1 \text{ M})^2(0.2 \text{ M})} = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} \)

\( k_2 = 150/(0.25)^2(0.20) = 1.20 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} \)

\( k_3 = 60/(0.10)^2(0.50) = 1.20 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} \)

\( k_4 = 735/(0.35)^2(0.50) = 1.2 \times 10^4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} \)

\( k_{\text{avg}} = (1.2 \times 10^4 + 1.2 \times 10^4 + 1.2 \times 10^4 + 1.2 \times 10^4 + 1.2 \times 10^4)/4 = 1.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} \)

(c) Use the reaction stoichiometry and Equation 14.4 to relate the designated rates. \( \frac{-\Delta[\text{Br}_2]}{\Delta t} = \frac{k[\text{NO}]^2[\text{Br}_2]}{2} \) the rate of disappearance of \( \text{Br}_2 \) is half the rate of appearance of \( \text{NOBr} \).

(d) Note that the data are given in terms of appearance of \( \text{NOBr} \).

\[ \frac{-\Delta[\text{Br}_2]}{\Delta t} = \frac{k[\text{NO}]^2[\text{Br}_2]}{2} = \frac{1.2 \times 10^4}{2 \text{ M}^2 \text{ s}} \times (0.07 \text{ M})^2 \times (0.025 \text{ M}) = 8.4 \text{ M/s} \]
Change of Concentration with Time

14.35 (a) 

\[ [A]_0 \] is the molar concentration of reactant A at time zero, the initial concentration of A. 
\[ [A]_t \] is the molar concentration of reactant A at time \( t \). 
\( t_{1/2} \) is the time required to reduce \([A]_0\) by a factor of 2, the time when 
\[ [A]_t = \frac{[A]_0}{2} \]. 
\( k \) is the rate constant for a particular reaction. \( k \) is independent of reactant concentration but varies with reaction temperature.

(b) A graph of \( \ln[A] \) vs time yields a straight line for a first-order reaction.

14.37 Analyze/Plan. The half-life of a first-order reaction depends only on the rate constant, 
\( t_{1/2} = \frac{0.693}{k} \). Use this relationship to calculate \( k \) for a given \( t_{1/2} \), and, at a different temperature, \( t_{1/2} \) given \( k \).

Solve.

(a) \( t_{1/2} = 2.3 \times 10^5 \) s; \( t_{1/2} = \frac{0.693}{k} \) 
\( k = \frac{0.693}{2.3 \times 10^5} = 3.0 \times 10^{-6} \) s\(^{-1} \)

(b) \( k = 2.2 \times 10^{-5} \) s\(^{-1} \). \( t_{1/2} = \frac{0.693}{2.2 \times 10^{-5}} = 3.15 \times 10^4 = 3.2 \times 10^4 \) s

14.39 Analyze/Plan. Follow the logic in Sample Exercise 14.7. In this reaction, pressure is a measure of concentration. In (a) we are given \( k \), \([A]_0 \), \( t \) and asked to find \([A]_t \) using Equation [14.13], the integrated form of the first-order rate law. In (b), \([A]_t = 0.1[A]_0\), find \( t \).

Solve.

(a) \( \ln P_t = -kt + \ln P_0 \); \( P_0 = 375 \) torr; \( t = 65 \) s
\( \ln P_{65} = -4.5 \times 10^{-2} \) s\(^{-1}\)(65) + \( \ln(375) = -2.925 + 5.927 = 3.002 \)
\( P_{65} = 20.12 = 20 \) torr

(b) \( P_t = 0.10 P_0 \); \( \ln(P_t/P_0) = -kt \)
\( \ln(0.10 P_0/P_0) = -kt; \ln(0.10) = -kt; -\ln(0.10)/k = t \)
\( t = \frac{-(-2.303)}{4.5 \times 10^{-2}} = 51.2 = 51 \) s

Check. From part (a), the pressure at 65 s is 20 torr, \( P_t \approx 0.05 P_0 \). In part (b) we calculate the time where \( P_t = 0.10 P_0 \) to be 51 s. This time should be smaller than 65 s, and it is. Data and results in the two parts are consistent.

14.41 Analyze/Plan. Given reaction order, various values for \( t \) and \( P_t \), find the rate constant for the reaction at this temperature. For a first-order reaction, a graph of \( \ln P \) vs \( t \) is linear with as slope of \(-k\). Solve.

<table>
<thead>
<tr>
<th>( t(s) )</th>
<th>( P_{SO_2Cl_2} )</th>
<th>( \ln P_{SO_2Cl_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
<td>0</td>
</tr>
<tr>
<td>2500</td>
<td>0.947</td>
<td>-0.0545</td>
</tr>
<tr>
<td>5000</td>
<td>0.895</td>
<td>-0.111</td>
</tr>
<tr>
<td>7500</td>
<td>0.848</td>
<td>-0.165</td>
</tr>
</tbody>
</table>

Check.
Graph \( \ln P_{\text{SO}_2\text{Cl}_2} \) vs. time. (Pressure is a satisfactory unit for a gas, since the concentration in moles/liter is proportional to \( P \).) The graph is linear with slope \(-2.19 \times 10^{-5} \text{ s}^{-1}\) as shown on the figure. The rate constant \( k = -\text{slope} = 2.19 \times 10^{-5} \text{ s}^{-1} \).

### 14.43 Analyze/Plan

Given: mol A, \( t \). Change mol to \( M \) at various times. Make both first- and second-order plots to see which is linear. 

#### Solve

(a) 
<table>
<thead>
<tr>
<th>time(min)</th>
<th>mol A</th>
<th>[A] (M)</th>
<th>\ln[A]</th>
<th>1/mol A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.065</td>
<td>0.65</td>
<td>-0.43</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>0.051</td>
<td>0.51</td>
<td>-0.67</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>0.042</td>
<td>0.42</td>
<td>-0.87</td>
<td>2.4</td>
</tr>
<tr>
<td>30</td>
<td>0.036</td>
<td>0.36</td>
<td>-1.02</td>
<td>2.8</td>
</tr>
<tr>
<td>40</td>
<td>0.031</td>
<td>0.31</td>
<td>-1.17</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The plot of \( 1/[A] \) vs time is linear, so the reaction is second-order in \([A]\). 

(b) For a second-order reaction, a plot of \( 1/[A] \) vs. \( t \) is linear with slope \( k \).

\[
    k = \text{slope} = (3.2 - 2.0) M^{-1}/30 \text{ min} = 0.040 \text{ M}^{-1} \text{ min}^{-1}
\]

(The best fit to the line yields slope = 0.042 \text{ M}^{-1} \text{ min}^{-1}.)

(c) \( t_{1/2} = 1/k[A]_0 = 1/(0.040 \text{ M}^{-1} \text{ min}^{-1})(0.65 \text{ M}) = 38.46 = 38 \text{ min} \)

(Using the “best-fit” slope, \( t_{1/2} = 37 \text{ min} \).)

### 14.45 Analyze/Plan

Follow the logic in Solution 14.43. Make both first and second order plots to see which is linear. 

#### Solve

(a) 
<table>
<thead>
<tr>
<th>time(s)</th>
<th><a href="M">NO(_2)</a></th>
<th>\ln[NO(_2)]</th>
<th>1/[NO(_2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.100</td>
<td>-2.303</td>
<td>10.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.017</td>
<td>-4.08</td>
<td>59</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0090</td>
<td>-4.71</td>
<td>110</td>
</tr>
<tr>
<td>15.0</td>
<td>0.0062</td>
<td>-5.08</td>
<td>160</td>
</tr>
</tbody>
</table>
The plot of \(1/\text{[NO}_2\text{]}\) vs time is linear, so the reaction is second order in NO\(_2\).

(b) The slope of the line is \((210 - 59) M^{-1}/15.0 \text{ s} = 10.07 = 10 M^{-1}s^{-1} = \text{k. (The slope of the best-fit line is 10.02 = 10 M}^{-1}s^{-1}).

Temperature and Rate

14.47 (a) The energy of the collision and the orientation of the molecules when they collide determine whether a reaction will occur.

(b) According to the kinetic-molecular theory (Chapter 10), the higher the temperature, the greater the speed and kinetic energy of the molecules. Therefore, at a higher temperature, there are more total collisions and each collision is more energetic.

14.49 Analyze/Plan. Given the temperature and energy, use Equation [14.18] to calculate the fraction of Ar atoms that have at least this energy. Solve.

\[ f = e^{\frac{-E_a}{RT}} \]

\[ E_a = 10.0 \text{ kJ/mol} = 1.00 \times 10^4 \text{ J/mol}; T = 400 \text{ K (127°C)} \]

\[ -\frac{E_a}{RT} = -\frac{1.00 \times 10^4 \text{ J/mol}}{400K} \times \frac{\text{mol} \cdot K}{8.314} = -3.0070 \cdot 3.0 \]

\[ f = e^{3.0070} = 4.9 \times 10^{-2} \]

At 400 K, approximately 1 out of 20 molecules has this kinetic energy.

14.51 Analyze/Plan. Use the definitions of activation energy \((E_{\text{max}} - E_{\text{react}})\) and \(\Delta E\) \((E_{\text{prod}} - E_{\text{react}})\) to sketch the graph and calculate \(E_a\) for the reverse reaction. Solve.

(a) \(E_a = 7 \text{ kJ}\)

(b) \(E_a(\text{reverse}) = 73 \text{ kJ}\)
14.53 Assuming all collision factors (A) to be the same, reaction rate depends only on \( E_a \); it is independent of \( \Delta E \). Based on the magnitude of \( E_a \), reaction (b) is fastest and reaction (c) is slowest.

14.55 Analyze/Plan. Given \( k_1 \), at \( T_1 \), calculate \( k_2 \) at \( T_2 \). Change T to Kelvins, then use the Equation \([14.21]\) to calculate \( k_2 \). Solve.

\[
T_1 = 20^\circ C + 273 = 293 \text{ K}; \quad T_2 = 60^\circ C + 273 = 333 \text{ K}; \quad k_1 = 2.75 \times 10^{-2} \text{ s}^{-1}
\]

\[
(a) \quad \ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{333} - \frac{1}{293} \right) = 75.5 \times 10^3 \text{ J/mol} \times \frac{8.314 \text{ J/mol}}{(-4.100 \times 10^{-4})} = -3.722 \text{ } - 3.7; k_1/k_2 = 0.0242 \quad 0.0242 = 1.14 \times 1 \text{ s}^{-1}
\]

\[
(b) \quad \ln \left( \frac{k_1}{k_2} \right) = \frac{125 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}} \times \left( \frac{1}{333} - \frac{1}{293} \right) = -6.163 \quad 6.2
\]

\[
k_1/k_2 = 2.104 \times 10^3 = 2 \times 10^3; \quad k_2 = \frac{0.027 \text{ s}^{-1}}{2.104 \times 10^3} = 13.0 \times 1 \times 1 \text{ s}^{-1}
\]


\[
\begin{array}{c|c|c|c}
 k & \ln k & T(\text{K}) & 1/T(\times 10^3) \\
\hline
0.0521 & -2.955 & 288 & 3.47 \\
0.101 & -2.293 & 298 & 3.36 \\
0.184 & -1.693 & 308 & 3.25 \\
0.332 & -1.103 & 318 & 3.14 \\
\end{array}
\]

The slope, \(-5.71 \times 10^3\), equals \(-E_a/R\). Thus, \( E_a = 5.71 \times 10^3 \times 8.314 \text{ J/mol} = 47.5 \text{ kJ/mol} \).

14.59 Analyze/Plan. Given \( E_a \), find the ratio of rates for a reaction at two temperatures. Assuming initial concentrations are the same at the two temperatures, the ratio of rates will be the ratio of rate constants, \( k_1/k_2 \). Use Equation \([14.21]\) to calculate this ratio. Solve.

\[
T_1 = 50^\circ C + 273 = 323 \text{ K}; \quad T_2 = 0^\circ C + 273 = 273 \text{ K}
\]

\[
\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{65.7 \text{ kJ/mol}}{8.314 \text{ J/mol} \times 1 \text{ kJ}} \left[ \frac{1}{273} - \frac{1}{323} \right]
\]

\[
\ln \left( \frac{k_1}{k_2} \right) = 7.902 \times 10^3 \times (5.670 \times 10^{-4}) = 4.481 = 4.5; \quad k_1/k_2 = 88.3 = 9 \times 10^1
\]

The reaction will occur 90 times faster at 50°C, assuming equal initial concentrations.

Reaction Mechanisms

14.61 (a) An elementary reaction is a process that occurs in a single event; the order is given by the coefficients in the balanced equation for the reaction.
(b) A unimolecular elementary reaction involves only one reactant molecule; the activated complex is derived from a single molecule. A bimolecular elementary reaction involves two reactant molecules in the activated complex and the overall process.

(c) A reaction mechanism is a series of elementary reactions that describe how an overall reaction occurs and explain the experimentally determined rate law.

### 14.63 Analyze/Plan

Elementary reactions occur as a single step, so the molecularity is determined by the number of reactant molecules; the rate law reflects reactant stoichiometry. Solve.

(a) unimolecular, rate = \( k[Cl_2] \)

(b) bimolecular, rate = \( k[OCl][H_2O] \)

(c) bimolecular, rate = \( k[NO][Cl_2] \)

### 14.65 Analyze/Plan

Use the definitions of the terms ‘intermediate’ and ‘exothermic’, along with the characteristics of reaction profiles, to answer the questions. Solve.

This is a three-step mechanism, \( A \rightarrow B \), \( B \rightarrow C \), and \( C \rightarrow D \).

(a) There are 2 intermediates, B and C.

(b) There are 3 energy maxima in the reaction profile, so there are 3 transition states.

(c) Step \( C \rightarrow D \) has the lowest activation energy, so it is fastest.

(d) The energy of \( D \) is slightly greater than the energy of \( A \), so the overall reaction is endothermic.

### 14.67

(a) \( H_2(g) + ICl(g) \rightarrow HI(g) + HCl(g) \)

\( HI(g) + ICl(g) \rightarrow I_2(g) + HCl(g) \)

\( H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g) \)

(b) Intermediates are produced and consumed during reaction. HI is the intermediate.

(c) Follow the logic in Sample Exercise 14.13.

First step: rate = \( k_1[H_2][ICl] \)

Second step: rate = \( k_2[HI][ICl] \)

(d) The slow step determines the rate law for the overall reaction. If the first step is slow, the observed rate law is: rate = \( k[H_2][HCl] \).

### 14.69 Analyze/Plan

Given a proposed mechanism and an observed rate law, determine which step is rate determining. Solve.

(a) If the first step is slow, the observed rate law is the rate law for this step.

rate = \( k[NO][Cl_2] \)

(b) Since the observed rate law is second-order in [NO], the second step must be slow relative to the first step; the second step is rate determining.
Catalysis

14.71 (a) A catalyst increases the rate of reaction by decreasing the activation energy, $E_a$, or increasing the frequency factor $A$. Lowering the activation energy is more common and more dramatic.

(b) A homogeneous catalyst is in the same phase as the reactants; a heterogeneous catalyst is in a different phase and is usually a solid.

14.73 (a) $2[\text{NO}_2(g) + \text{SO}_2(g) \rightarrow \text{NO}(g) + \text{SO}_3(g)]$

$2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

$2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$

(b) $\text{NO}_2(g)$ is a catalyst because it is consumed and then reproduced in the reaction sequence. ($\text{NO}(g)$ is an intermediate because it is produced and then consumed.)

(c) Since $\text{NO}_2$ is in the same state as the other reactants, this is homogeneous catalysis.

14.75 (a) Use of chemically stable supports such as alumina and silica makes it possible to obtain very large surface areas per unit mass of the precious metal catalyst. This is so because the metal can be deposited in a very thin, even monomolecular, layer on the surface of the support.

(b) The greater the surface area of the catalyst, the more reaction sites, and the greater the rate of the catalyzed reaction.

14.77 As illustrated in Figure 14.21, the two C–H bonds that exist on each carbon of the ethylene molecule before adsorption are retained in the process in which a D atom is added to each C (assuming we use $\text{D}_2$ rather than $\text{H}_2$). To put two deuteriums on a single carbon, it is necessary that one of the already existing C–H bonds in ethylene be broken while the molecule is adsorbed, so the H atom moves off as an adsorbed atom, and is replaced by a D. This requires a larger activation energy than simply adsorbing $\text{C}_2\text{H}_4$ and adding one D atom to each carbon.

14.79 (a) Living organisms operate efficiently in a very narrow temperature range; heating to increase reaction rate is not an option. Therefore, the role of enzymes as homogeneous catalysts that speed up desirable reactions without heating and undesirable side-effects is crucial for biological systems.

(b) $\text{catalase: } 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$; $\text{nitrogenase: } \text{N}_2 \rightarrow 2\text{NH}_3$ (nitrogen fixation)

14.81 Analyze/Plan. Let $k$ = the rate constant for the uncatalyzed reaction, $k_c$ = the rate constant for the catalyzed reaction

According to Equation [14.20], $\ln k = -E_a / RT + \ln A$

Subtracting $\ln k$ from $\ln k_c$,

$$\ln k_c - \ln k = - \left[ \frac{55 \text{kJ/mol}}{RT} + \ln A \right] - \left[ - \frac{95 \text{kJ/mol}}{RT} + \ln A \right].$$ 

Solve
14 Chemical Kinetics  Solutions to Exercises

(a) \[ RT = 8.314 \text{ J/K-mol} \times 298 \text{ K} \times 1 \text{ kJ/1000 J} = 2.478 \text{ kJ/mol} \text{; ln } A \text{ is the same for both reactions.} \]

\[ \ln \left( \frac{k_c}{k} \right) = \frac{95 \text{ kJ/mol} - 55 \text{ kJ/mol}}{2.478 \text{ J/mol}} \text{; } k_c/k = 1.024 \times 10^6 = 1 \times 10^7 \]

The catalyzed reaction is approximately 10,000,000 (ten million) times faster at 25°C.

(b) \[ RT = 8.314 \text{ J/K - mol} \times 398 \text{ K} \times 1 \text{ kJ/1000 J} = 3.309 \text{ kJ/mol} \]

\[ \ln \left( \frac{k_c}{k} \right) = \frac{40 \text{ kJ/mol}}{3.309 \text{ J/mol}} \text{; } k_c/k = 1.778 \times 10^7 = 2 \times 10^7 \]

The catalyzed reaction is 200,000 times faster at 125°C.

Additional Exercises

14.83 A balanced chemical equation shows the overall, net change of a chemical reaction. Most reactions occur as a series of (elementary) steps. The rate law contains only those reactants that form the transition state of the rate-determining step. If a reaction occurs in a single step, the rate law can be written directly from the balanced equation for the step.

14.86 (a) The rate increases by a factor of nine when \([C_2O_4^{2–}]\) triples (compare experiments 1 and 2). The rate doubles when \([\text{HgCl}_2]\) doubles (compare experiments 2 and 3). The rate law is apparently: rate = \(k[\text{HgCl}_2][C_2O_4^{2–}]^3\)

(b) \(k = \frac{\text{rate}}{[\text{HgCl}_2][C_2O_4^{2–}]^2}\) Using the data for Experiment 1,

\[ k = \frac{(3.2 \times 10^5 \text{ M/s})}{\left(0.16M\right)^2\left(0.19M\right)^2} = 8.672 \times 10^3 = 8.7 \times 10^3 \text{ M}^{-2}\text{s}^{-1} \]

(c) \(\text{rate} = (8.672 \times 10^{-3} \text{ M}^{-2}\text{s}^{-1})(0.100 \text{ M})(0.25 \text{ M})^2 = 5.4 \times 10^{-5} \text{ M/s} \)

14.89 (a) \(t_{1/2} = 0.693/k = 0.693/7.0 \times 10^{-4} \text{ s}^{-1} = 990 = 9.9 \times 10^2 \text{ s} \)

(b) \(k = \frac{0.693}{t_{1/2}} = \frac{0.693}{56.3 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.05 \times 10^{-4} \text{ s}^{-1} \)

14.92 (a) \(A = abc\), Equation [14.5]. \(A = 0.605\), \(a = 5.60 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}\), \(b = 1.00 \text{ cm}\)

\[ c = \frac{A}{ab} = \frac{0.605}{(5.60 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})} = 1.080 \times 10^4 = 1.08 \times 10^4 \text{ M} \]

(b) Calculate \([c]\), using Beer’s law. We calculated \([c]_0\) in part (a). Use Equation [14.13] to calculate \(k\).

\[ A_{30} = abc_0c_{30} = \frac{A_{30}}{ab} = \frac{0.250}{(5.60 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})} = 4.464 \times 10^5 \text{ M} \]

\[ \ln[c] = -kt + \ln[c]_0; \frac{\ln[c]_0 - \ln[c]}{t} = k; t = 30 \text{ min} \times \frac{60 \text{ s}}{\text{min}} = 1800 \text{ s} \]

\[ k = \ln(1.080 \times 10^{-4}) - \ln(4.464 \times 10^{-5}) / 1800 \text{ s} = 4.910 \times 10^{-4} = 4.91 \times 10^{-4} \text{ s}^{-1} \]

(c) For a first order reaction, \(t_{1/2} = 0.693/k\).
14 Chemical Kinetics

Solutions to Exercises

\[ t_{1/2} = 0.693/4.910 \times 10^{-4} \text{ s}^{-1} = 1.411 \times 10^3 = 1.41 \times 10^3 \text{ s} = 23.5 \text{ min} \]

(d) \( A_t = 0.100; \) calculate \( c_t \) using Beer’s law, then \( t \) from the first order integrated rate equation.

\[
c_t = \frac{A}{ab} = \frac{0.100}{(5.60 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})} = 1.78 \times 10^{-5} = 1.79 \times 10^{-5} \text{ M} \\
t = \frac{\ln[c_f] - \ln[c]}{k} = \frac{\ln(1.08 \times 10^4) - \ln(1.78 \times 10^5)}{4.910 \times 10^4 \text{ s}^{-1}} \\
t = 3.666 \times 10^3 = 3.67 \times 10^3 \text{ s} = 61.1 \text{ min} \\

14.95

\begin{array}{cc}
\text{ln } k & 1/T \\
-24.17 & 3.33 \times 10^{-3} \\
-20.72 & 3.13 \times 10^{-3} \\
-17.32 & 2.94 \times 10^{-3} \\
-15.24 & 2.82 \times 10^{-3} \\
\end{array}

The calculated slope is \(-1.751 \times 10^4\). The activation energy \( E_a \) equals \(-\text{(slope)} \times (8.314 \text{ J} / \text{mol})\). Thus, \( E_a = 1.8 \times 10^5 \times (8.314) = 1.5 \times 10^5 \text{ J} / \text{mol} = 1.5 \times 10^2 \text{ kJ} / \text{mol} \). (The best-fit slope is \(-1.76 \times 10^4 \) and the value of \( E_a \) is \( 1.5 \times 10^2 \text{ kJ} / \text{mol} \).)

14.99

(a) \( \text{Cl}_2(g) \rightarrow 2\text{Cl}(g) \)

\[
\text{Cl}(g) + \text{CHCl}_3(g) \rightarrow \text{HCl}(g) + \text{CCl}_3(g) \\
\text{Cl}(g) + \text{CCl}_3(g) \rightarrow \text{CCl}_4(g) \\
\text{Cl}_2(g) + 2\text{Cl}(g) + \text{CHCl}_3(g) + \text{CCl}_3(g) \rightarrow 2\text{Cl}(g) + \text{HCl}(g) + \text{CCl}_3(g) + \text{CCl}_4(g) \\
\text{Cl}_2(g) + \text{CHCl}_3(g) \rightarrow \text{HCl}(g) + \text{CCl}_4(g)
\]

(b) \( \text{Cl}(g), \text{CCl}_3(g) \)

(c) Reaction 1 - unimolecular, Reaction 2 - bimolecular, Reaction 3 - bimolecular

(d) Reaction 2, the slow step, is rate determining.

(e) If Reaction 2 is rate determining, \( \text{rate} = k_2[\text{CHCl}_3][\text{Cl}] \). \( \text{Cl} \) is an intermediate formed in reaction 1, an equilibrium. By definition, the rates of the forward and reverse processes are equal; \( k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2 \). Solving for \([\text{Cl}]\) in terms of \([\text{Cl}_2]\),

\[
[\text{Cl}]^2 = \frac{k_1}{k_{-1}} [\text{Cl}_2]; \quad [\text{Cl}] = \left( \frac{k_1}{k_{-1}} [\text{Cl}_2] \right)^{1/2}
\]

Substituting into the overall rate law

\[
\text{rate} = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{CHCl}_3][\text{Cl}_2]^{1/2} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2} \text{ (The overall order is 3/2.)}
\]

390
14 Enzyme: carbonic anhydrase; substrate: carbonic acid (H$_2$CO$_3$); turnover number: $1 \times 10^7$ molecules/s.

Integrative Exercises

14.104 **Analyze/Plan.** $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ rate = $k[\text{N}_2\text{O}_5] = 1.0 \times 10^{-5}$ s$^{-1}$ [N$_2$O$_5$]

Use the integrated rate law for a first-order reaction, Equation [14.13], to calculate $k[\text{N}_2\text{O}_5]$ at 20.0 hr. Build a stoichiometry table to determine mol O$_2$ produced in 20.0 hr. Assuming that O$_2$(g) is insoluble in chloroform, calculate the pressure of O$_2$ in the 10.0 L container. **Solve.**

\[
\ln[A]_t - \ln[A]_0 = -kt; \ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_0
\]

\[
\ln [\text{N}_2\text{O}_5]_t = -1.0 \times 10^{-5}$ s$^{-1}$ (7.20 $\times$ 10$^4$ s) + ln(0.600) = -0.720 - 0.511 = -1.231
\]

\[
[N_2O_5]_t = e^{-1.231} = 0.292 \text{ M}
\]

N$_2$O$_5$ was present initially as 1.00 L of 0.600 M solution.

mol N$_2$O$_5$ = M $\times$ L = 0.600 mol N$_2$O$_5$ initial, 0.292 mol N$_2$O$_5$ at 20.0 hr

\[
2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2
\]

\begin{align*}
t &= 0 & 0.600 \text{ mol} & 0 & 0 \\
\text{change} & & -0.308 \text{ mol} & 0.616 \text{ mol} & 0.154 \text{ mol} \\
t &= 20 \text{ hr} & 0.292 \text{ mol} & 0.616 \text{ mol} & 0.154 \text{ mol}
\end{align*}

[Note that the reaction stoichiometry is applied to the ‘change’ line.]

PV = nRT; $P = nRT/V$; $V = 10.0$ L, $T = 45^\circ$C = 318 K, $n = 0.154$ mol

\[
P = 0.154 \text{ mol} \times \frac{318 \text{ K}}{10.0 \text{ L}} \times \frac{0.082056 \text{ atm}}{\text{mol} \cdot \text{K}} = 0.402 \text{ atm}
\]

14.106 (a) Use an apparatus such as the one pictured in Figure 10.3 (an open-end manometer), a clock, a ruler and a constant temperature bath. Since $P = (n/V)RT$, $\Delta P/\Delta t$ at constant temperature is an acceptable measure of reaction rate.

Load the flask with HCl(aq) and read the height of the Hg in both arms of the manometer. Quickly add Zn(s) to the flask and record time = 0 when the Zn(s) contacts the acid. Record the height of the Hg in one arm of the manometer at convenient time intervals such as 5 sec. (The decrease in the short arm will be the same as the increase in the tall arm). Calculate the pressure of H$_2$(g) at each time.

(b) Keep the amount of Zn(s) constant and vary the concentration of HCl(aq) to determine the reaction order for H$^+$ and Cl$^-$. Keep the concentration of HCl(aq) constant and vary the amount of Zn(s) to determine the order for Zn(s). Combine this information to write the rate law.

(c) $-\Delta[H^+]/2\Delta t = \Delta[H_2]/\Delta t$; $-\Delta[H^+]/\Delta t = 2\Delta[H_2]/\Delta t$
\[ [H_2] = \text{mol} H_2/L = n/V; [H_2] = P \text{ (in atm)}/RT \]

Then, the rate of disappearance of $H^+$ is twice the rate of appearance of $H_2(g)$.

(d) By changing the temperature of the constant temperature bath, measure the rate data at several (at least three) temperatures and calculate the rate constant $k$ at these temperatures. Plot $\ln k$ vs $1/T$. The slope of the line is $-E_a/R$ and $E_a = -\text{slope (R)}$.

(e) Measure rate data at constant temperature, HCl concentration and mass of Zn(s), varying only the form of the Zn(s). Compare the rate of reaction for metal strips and granules.

14.109 In the lock and key model of enzyme action, the active site is the specific location in the enzyme where reaction takes place. The precise geometry (size and shape) of the active site both accommodates and activates the substrate (reactant). Proteins are large biopolymers, with the same structural flexibility as synthetic polymers (Chapter 12). The three-dimensional shape of the protein in solution, including the geometry of the active site, is determined by many intermolecular forces of varying strengths.

Changes in temperature change the kinetic energy of the various groups on the enzyme and their tendency to form intermolecular associations or break free from them. Thus, changing the temperature changes the overall shape of the protein and specifically the shape of the active site. At the operating temperature of the enzyme, the competition between kinetic energy driving groups apart and intermolecular attraction pulling them together forms an active site that is optimum for a specific substrate. At temperatures above the temperature of maximum activity, sufficient kinetic energy has been imparted so that the forces driving groups apart win the competition, and the three-dimensional structure of the enzyme is destroyed. This is the process of denaturation. The activity of the enzyme is destroyed because the active site has collapsed. The protein or enzyme is denatured, because it is no longer capable of its “natural” activity.

$\text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2$ is a termination step.